PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

EFFERT, BRESSEL UND KOLLEGEN
Radickestrasse 48
D-12489 Berlin
ALLEMAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	26.10.2004
Applicant's or agent's file reference	**IMPORTANT NOTIFICATION**
P60156PCT	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP 03/09030	14.08.2003	28.08.2002

Applicant
ATOTECH DEUTSCHLAND GMBH et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Ipinazar, P Tel. +49 89 2399-8131

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P60156PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/09030	International filing date *(day/month/year)* 14.08.2003	Priority date *(day/month/year)* 28.08.2002
International Patent Classification (IPC) or both national classification and IPC C23C18/16		
Applicant ATOTECH DEUTSCHLAND GMBH et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

I	☒	Basis of the opinion
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain documents cited
VII	☐	Certain defects in the international application
VIII	☐	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
13.02.2004	26.10.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Goers, B Telephone No. +49 89 2399-7343

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/09030

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-31 as originally filed

Claims, Numbers

1-12 filed with telefax on 01.10.2004

Drawings, Sheets

1/2-2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

1 Reference is made to the following documents:

D1: WO 00 23637 A (RICHTERING WERNER ;BORN RAINER (DE); HEYDECKE JENS (DE); WUENSCHE) 27 April 2000 (2000-04-27) cited in the application

D2: WO 94 12439 A (MONSANTO CO) 9 June 1994 (1994-06-09)

D3: FR-A-2 189 523 (HAGER & ELSAESSER) 25 January 1974 (1974-01-25)

D4: US-B-6 245 3891 (TASHIRO KATSUHIRO ET AL) 12 June 2001 (2001-06-12)

D5: DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; RENZ R P ET AL: "In-process recycling of a hexavalent chromium plating bath" XP002260386 Database accession no. EIX99454777298

D6: DE 198 51 180 C (HAHNEWALD GMBH ;GUV GES FUER UMWELTVERTRAEGLIC (DE)) 20 April 2000 (2000-04-20)

2 The amendments filed with the letter of 14.10.04 fulfill the requirements of Article 34(2)(b) PCT.

3 Article 33(3) PCT

3.1 The features of the nickel plating bath regeneration device within **apparatus claim 1 and method claim 7** of the applications are as follows:

i) an electrodialysis arrangement for the transfer of interfering substances from the diluate to the concentrate compartments,

ii) collection tanks,

iii) a cation exchanger in the recirculation circuit of the concentrate suitable to capture metal ions (cf. D6, fig. 3, ref. T2),

iv) a first recirculation circuit between the concentrate compartments of I) and tanks ii) and

v) a second recirculation circuit between the tanks ii) and cation exchanger iii)

3.2 **Closest prior art** document D6 discloses a method of regeneration of an electroless nickel plating bath comprising and electrodialysis device, an anion exchanger (fig. 3, T1) in the concentrate circuit and a cation exchanger (T2) fed by a side stream of said circuit and discharging in the diluate compartments.

The difference is that no collection tanks and the respective circuit are disclosed (features ii) and v)) and further that the effluent of the cation exchanger is not fed back to the concentrate circuit.

3.3 The **problem to be solved** is to maintain a low metal concentration at the concentrate side in order to avoid to prevent autocatalytic decomposition of the solution while setting a cross-flow in the concentration compartments adapted for

the optimised transmembrane mass transfer of interfering substances (cf. argumentation with letter of 14.10.04).

3.4 **The solution** is to introduce a recycle of concentrate which was metal depleted by means of the cation exchanger (realised by feature iv) while decoupling the recirculation flowrate in the concentration compartment by means of arranging the ion exchanger in a separate circuit (v). In circuit iv) a recirculation rate suitable for enhancing the mass transfer of interfering components can be realized while the recirculation rate in circuit v) is adapted for setting a desired nickel depletion of circuit vi). The hydraulic connection is established by tank ii).

3.5 According to D6, col. 4, ll 17-35, the cation exchanger (the anion exchanger is not of interest here as it is directed to the removal of the interfering component) is introduced in order to spent nickel ions to the processing liquid and not to capture nickel ions having passed into the concentration compartment. It is thus not possible to directly influence the nickel concentration in the concentrate circuit by means of the ion exchanger. Of course a continuous withdrawal of circuit liquid via T2 will also effect the nickel concentration in the circuit. However the withdrawal affords in addition a makeup stream for the concentrate liquid.

3.6 Combination with the other documents cited
D1 does simply disclose an electrodialysis process for the regeneration of plating bath solution.

D2 is dealing with a method for regenerating a copper electroless plating bath by separating monovalent species via a monoselective nanofiltration membrane (p. 4, l. 9-35). As the separation efficiency for the heavy metal chelate is not 100%, the residual heavy metal chelates are captured by an ion exchanger device on the permeate side and later on recycled back to the bath (D2, claim 8). Thus no concentrate circuit with an ion exchanger is disclosed.

D3 only mentions the possibility of further concentrating specific unwanted components (like nickel) resulting from the retentate of a reverse osmosis step by means of an ion exchanger and later on recycle the components into the bath. No concentrate circuit is disclosed.

D4 discloses an ion exchange pretreatment for the eletrodialysis step.

D5 combines an electrodialysis device with cation exchange resin within the concentrate channel. Although the ion exchanger thus is introduced in the concentrate circuit, no means for the decoupling by means of a second circuit is envisaged.

3.7 The solution as suggested by the subject matter of apparatus claim 1 and process claim 7 is not derivable from D6 nor is it obvious from a combination with any of the documents D1-D5. It is thus regarded to fulfil the requirements of Article 33(2)&(3) PCT.

Re Item IIIV

I The wording of claim 9 is not clear with respect to which fluid is to be recirculated to the collection tanks. It was interpreted to mean "concentrate fluid ... is displaced by the regenerant fluid for regeneration and **the concentrate fluid** is recirculated back into the collection tanks (V_K)".

10/524737
DT01 Rec'd PCT/PTC 16 FEB 2005

PCT/EP03/09030
Atotech Deutschland GmbH
14 October 2004

Patent Claims:

1. A device for regenerating an electroless metal plating bath, comprising

a) electrodialysis arrangements (E1, E2), each having diluate compartments (Di1y, Di2y) for holding the metal plating bath, concentrate compartments (Ko1y, Ko2y) that are separated from the diluate compartments (Di1y, Di2y) through ion exchange membranes and are intented to hold a concentrate fluid serving to adsorb interfering substances that are to be removed from the metal plating bath as well as anodes (An) and cathodes (Ka), and

b) main cation exchangers (I_x) for removing metal ions from the concentrate fluid, said cation exchangers being coupled to the concentrate compartments (Ko1y, Ko2y) in such a manner that the concentrate fluid is allowed to be conducted through the main cation exchangers (I_x) and to be recirculated back into the concentrate compartments (Ko1y, Ko2y) by allowing the fluid to be circulated in a first circuit between the concentrate compartments (Ko1y, Ko2y) and collecting tanks (V_k) and in a second circuit between the collecting tanks (V_k) and the main cation exchangers (I_x).

2. The device according to claim 1, wherein said device is comprised of

a) a first electrodialysis arrangement (E1) having alternating concentrate compartments (Ko1y) and diluate compartments (Di1y) as well as cathodes (Ka) and anodes (An), the diluate compartments (Di1y) being each separated on the cathode side

thereof from a neighbouring concentrate compartment (Ko1y) by a monoselective cation exchange membrane (KS) and on the anode side thereof from a neighbouring concentrate compartment (Ko1y) by an anion exchange membrane (A),

b) a second electrodialysis arrangement (E2) having alternating diluate compartments (Di2y) and concentrate compartments (Ko2y) as well as cathodes (Ka) and anodes (An), the concentrate compartments (Ko2y) being each separated on the cathode side thereof from a neighbouring diluate compartment (Di2y) by an anion exchange membrane (A) and on the anode side thereof from a neighbouring diluate compartment (Di2y) by a monoselective anion exchange membrane (AS),
so that the metal plating bath can be conducted simultaneously through all of the diluate compartments (Di1y, Di2y) in the two electrodialysis arrangements (E1, E2), the arrangements being connected in parallel, and the concentrate fluid being conducted through all of the concentrate compartments (Ko1y, Ko2y) in the two electrodialysis arrangements (E1, E2), and

c) current supplies (S) for the cathodes (Ka) and the anodes (An) of the first electrodialysis arrangement (E1) and of the second electrodialysis arrangement (E2).

3. The device according to any one of the preceding claims, wherein first regenerant fluid vessels (V_{RS1}) for holding regenerant fluid intended for the regeneration of the main cation exchangers (I_X) are further provided, said vessels being coupled to the main cation exchangers (I_X).

4. The device according to any one of the preceding claims, wherein service reservoirs (V_{ZK}) for holding concentrate fluid are further provided, said reservoirs being coupled to the collecting tanks (V_K) and to the main cation exchangers (I_X).

5. The device according to any one of the preceding claims, wherein safety cation exchangers (I_S) are further provided, said exchangers being coupled to the main cation exchangers (I_X) for post-treatment of the concentrate fluid treated in the main cation exchangers (I_X).

6. The device according to any one of the preceding claims, wherein second regenerant fluid vessels (V_{RSZ}) for holding regenerant fluid intended for the regeneration of the safety cation exchangers (I_s) are provided.

7. A method for regenerating an electroless metal plating bath, comprising

a) conducting the metal plating bath through the respective diluate compartments (Di1y, Di2y) of electrodialysis arrangements (E1, E2) and
b) conducting a concentrate fluid, serving to adsorb interfering substances that are to be removed from the metal plating bath, through respective concentrate compartments (Ko1y, Ko2y) of the electrodialysis arrangements (E1, E2), said concentrate compartments being separated from the diluate compartments (Di1y, Di2y) by ion exchange membranes,
c) moreover passing the concentrate fluid through main cation exchangers (I_X) and recirculating the fluid back into the concentrate compartments (Ko1y, Ko2y) by circulating the concentrate fluid in a first circuit between the concentrate compartments (Ko1y, Ko2y) and collecting tanks (V_K) and in a second circuit between the collecting tanks and the main cation exchangers (I_x).

8. The method according to claim 7, wherein the metal plating bath

a) is conducted through diluate compartments (Di1y) in a first electrodialysis arrangement (E1) comprising alternating concentrate compartments (Ko1y) and diluate compartments (Di1y) as well as cathodes (Ka) and anodes (An), the diluate compartments (Di1y) being each separated on the cathode side thereof from a neighbouring

concentrate compartment (Ko1y) by a monoselective cation exchange membrane (KS) and on the anode side thereof from a neighbouring concentrate compartment (Ko1y) by an anion exchange membrane (A), and

b) through diluate compartments (Di2y) in a second electrodialysis arrangement (E2) comprising alternating the diluate compartments (Di2y) and concentrate compartments (Ko2y) as well as cathodes (Ka) and anodes (An), the concentrate compartments (Ko2y) being each separated on the cathode side thereof from a neighbouring diluate compartment (Di2y) by an anion exchange membrane (A) and on the anode side thereof from a neighbouring diluate compartment (Di2y) by a monoselective anion exchange membrane (AS), and

wherein the metal plating bath is simultaneously conducted through all of the diluate compartments (Di1y, Di2y) in the two electrodialysis arrangements (E1, E2), the arrangements being connected in parallel, and the concentrate fluid being conducted through all of the concentrate compartments (Ko1y, Ko2y) in the two electrodialysis equipments (E1, E2).

9. The method according to any one of claims 7 or 8, wherein, for regenerating the main cation exchangers (I_X), concentrate fluid contained in the main cation exchangers (I_X) is displaced by a regenerant fluid and is recirculated back into the collecting tanks (V_K), the main cation exchangers (I_X) being regenerated in the process.

10. The method according to claim 9, wherein the regenerant fluid is drawn from first regenerant fluid vessels (V_{RS1}) and is transferred to the main cation exchangers (I_X).

11. The method according to any one of claims 9 or 10, wherein the regenerant fluid is displaced by the concentrate fluid after regeneration of the main cation exchangers (I_X) is complete, the regenerant fluid being recirculated back into

12. The method according to any one of claims 7 - 11, wherein concentrate fluid flows through several main cation exchangers (I_X) at different times with the regenerant fluid being circulated through those main cation exchangers (I_X) through which the concentrate fluid is not circulating for regeneration thereof.